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NUMBER 11

SECONDARY RADIATION FROM X-RAY FILTERS

I. SINGLE-METAL FILTERS¹

By G. A. WRENSHALL² AND H. J. NICHOLS³

Abstract

Using an ionization chamber method, the intensity distribution and quality of forward transmitted secondary X-rays from filters of aluminium, copper, tin, and lead have been measured under standard operating conditions. Geometrical arrangements of X-ray tube, defining apertures, filter, and receiver commonly used in medical and industrial radiology are employed. Suggestions for minimizing the intensity of the secondary radiation reaching the receiver from single-metal filters are submitted.

Introduction

While considerable study has been made of the secondary X-radiation emitted from absorbing foils, most investigators have studied only the portion of the radiation emitted on the incident side of the foil (1, 4, pp. 121, 125, 142). There is, however, practical interest in information concerning the forward transmitted secondary radiation since the distribution, hardness, and intensity of this radiation relative to that of the primary beam is found to be of importance in X-ray therapy and radiography where filters are employed. Since the transmitted primary beam is generally of much greater intensity than the forward transmitted secondary radiation produced by it, it is difficult to make accurate measurements of that part of the secondary radiation mixed with the transmitted primary beam. For this reason the secondary radiation falling just outside of the transmitted primary beam was examined in this investigation.

Seemann (6) has made an experimental study of the intensity distribution of the forward transmitted secondary X-rays from a filter as a function of certain variables in the geometry of his apparatus, which was arranged to simulate the conditions actually encountered where X-ray filtration is used. He has compared his measurements with calculations based on certain assumptions concerning the origin of the secondary X-rays. However, his most interesting measurements designed to test these calculations were made, not with secondary X-rays produced by an absorbing filter, but with light scattered by a ground-glass screen and detected with a light meter. The present paper

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deals in part with the direct measurement of the intensity distribution of secondary X-rays for the geometrical arrangements of source, filter, and detector suggested by Seemann as well as for other arrangements that were felt to be of practical importance.

Experiment

The geometrical conditions (Arrangements I and II) of apparatus employed in this study are illustrated in Figs. 1a and 1b respectively. In Arrangement I the cross-section of the primary X-ray beam from source S is maintained at

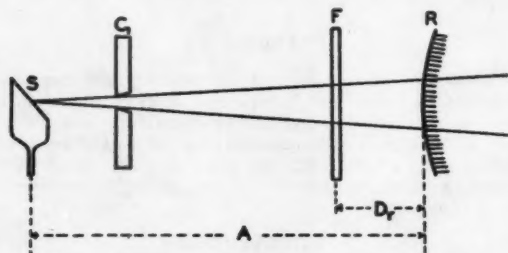


Fig. 1a.

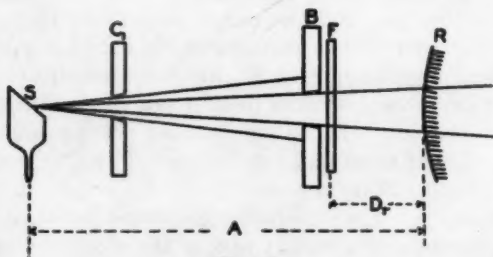


Fig. 1b.

FIGS. 1a AND 1b. Basic geometrical arrangements of X-ray source S , apertures, B , C_1 , filter, F , and receiver, R , as used in runs of Types I and II respectively.

constant size by a collimator, represented simply as C_1 . The primary beam is allowed to irradiate a receiver R placed at a constant distance A from S . The filter F , a foil of uniform thickness and sufficiently large in cross-section to fill the entire fixed cone of primary radiation at all positions, is inserted between S and R in a plane perpendicular to the direction SR . The intensity I_s of secondary radiation reaching R from F is then measured at various distances D_r of F from R . In Arrangement II, F is placed behind a lead aperture B , and the cross-section of the beam of primary X-rays is made sufficiently large to irradiate all of the exposed portion of F uniformly at all distances D_r of F from R , and D_r is varied with aperture B in contact with F in all positions.

The types of measurement made and reported in this paper are as follows:

- (a) Using Arrangement II, I_s is measured for various thicknesses of F , but with D , held constant, and for each of three peak voltages applied across the X-ray tube.
- (b) The space rate of absorption in aluminium of the secondary X-rays from F is measured, and the quality of the secondary radiation is ascertained therefrom. The apparatus is arranged as in (a), but with the addition of a variable number of aluminium plates of known mass per unit area interposed between F and W and parallel to F (Fig. 2). Each plate has a sufficiently large aperture at its centre to allow the primary beam of X-rays to pass through to C unaltered, while all secondary rays from F directed toward W have to pass through the plates. Absorption curves are obtained for the secondary X-rays reaching the ionization chamber from F , and effective absorption coefficients are estimated, the corresponding wave-lengths being obtained from physical tables.

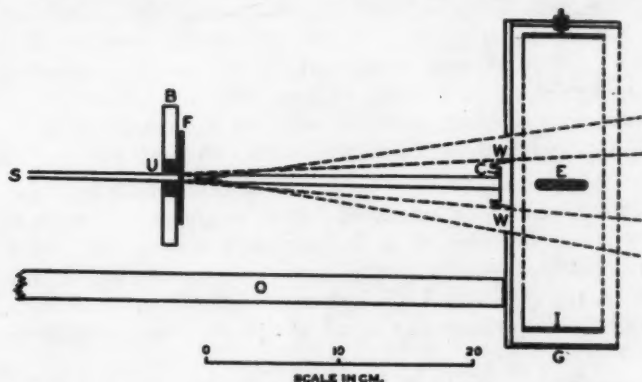


FIG. 2. Side section of the ionization chamber, and its position relative to filter F and optical bench O .

- (c) Using a set of rotating sectored lead disks to reduce the intensity of the primary beam by a known fraction, measurement is made of the relative intensities of primary and secondary X-rays reaching W from F using Arrangement II as in (a).
- (d) The observations made by Seemann are studied with X-rays for Arrangements I and II.

For the direct measurement of ionization of forward transmitted secondary X-rays in accordance with the geometrical conditions of Figs. 1a and 1b, the general disposition of apparatus shown schematically in Fig. 2 is employed. A collimated pencil of primary X-rays from a source S is allowed to pass through the absorbing filter F held against aperture B , and is finally blocked in a heavy lead cup C placed at the centre of the annular window W of a large flat cylindrical ionization chamber. Secondary X-rays originating in F enter and leave the inner ionization chamber I through aluminium foil windows,

relative intensities being measured by means of the saturation ionization current between I and the central electrode E , which is suitably connected to a completely shielded quadrant electrometer. Dry air at room temperature and pressure is used in I for all measurements, facilitating direct comparison of results with standard intensity measurements.

Both medium-focus and fine-focus Coolidge radiation type X-ray tubes (tungsten anticathodes) are used as sources, the latter being employed in all measurements of Type (d) where ideal geometrical conditions require the use of a point source of X-rays. The source S is completely encased in a lead box, and is supplied by a standard mechanical rectifier type of high tension supply whose peak kilovoltage output was measured under operating conditions by means of a standard sphere-gap. A storage battery source of filament current is used, making it possible to hold the intensity of the primary X-ray beam constant to within 1.0% during the course of an entire run.

Since it was found in preliminary runs that a considerable intensity of the secondary K-radiation of lead was reaching W from the edges of defining aperture B when 100 kvp. X-rays were employed, the periphery of this aperture was replaced by a plug U of uranium oxide and binder. This greatly improved the condition since the K-radiation of uranium is not excited by X-rays of less than 115 kv., while those of lead require only 88 kv.

The materials used successively in filter F , namely, lead, tin, copper, aluminium, are those commonly employed, either singly or in combination, by radiologists in the filtration of X-rays for medical purposes. Each was of the highest available degree of purity, and with respective atomic numbers of 82, 50, 29, 13, the results and conclusions obtained from the study of these metals should be representative of all metal elements available for filter construction.

Certain operations in the measurement of secondary X-ray intensities were common to all runs. After every measurement with a new filter setting, F was restored to a standard condition of thickness and position on the optical bench O , where the constancy of the primary beam intensity was checked*. Secondly, a correction was made by a single measurement for the general background radiation entering the ionization chamber in various ways, and for the unavoidable residuum of secondary radiation originating in U and entering W after passing through F . A foil of the same material and thickness as F was placed directly over W , and F was removed, following which the total background intensity was measured. In this way the secondary radiation from U had to penetrate the same thickness of filter material as before, and hence was reduced in intensity by the same fraction before entering W . General background radiation on the other hand, originating mainly in C as the secondary K-radiation of lead, or entering I through the thin rear windows, was relatively unchanged by this operation.

* In all measurements relative intensities of secondary X-rays were considered to be proportional to the unaccelerated rate of deflection of the electrometer needle over a fixed portion of the electrometer scale.

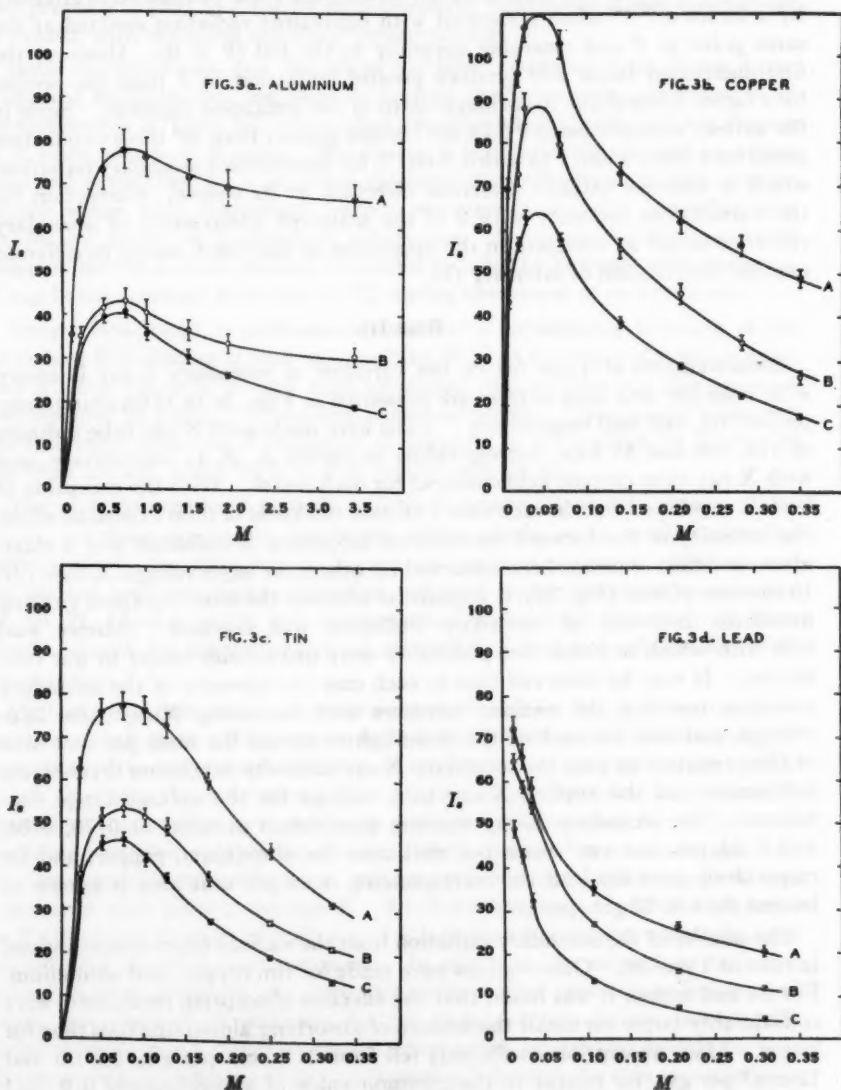
It will be observed from Fig. 2 that as F is moved along the axis of the primary X-ray beam, the mean angle θ , included between the primary beam axis and the secondary X-rays from F entering W , will vary between certain limits. Secondary radiation leaving F at an angle θ will be reduced in intensity by a factor $e^{-1/\cos\theta}$ when compared with equivalent radiation emitted at the same point in F and emerging normally to the foil ($\theta = 0$). However the first-mentioned beam will produce greater ionization in I than the second by a factor $1/\cos\theta$ due to its longer path in the ionization chamber. Since in the writers' measurements θ does not become greater than 10° these two factors annul each other's effect to within 0.001% for fluorescence secondary radiation, which is emitted without preferred direction at its source. Correction for the variation in intensity with θ of the scattered components of secondary radiation is not as complete in the apparatus as described, owing to different angular distribution of intensity (3).

Results

Measurements of Type (a) on the variation of secondary X-ray intensity with mass per unit area of filter are presented in Figs. 3a to 3d for aluminium, copper, tin, and lead respectively. Runs were made with X-ray tube voltages of 115, 100 and 85 kvp., corresponding to curves A, B, C, respectively, and with X-ray tube current held constant for each metal. With the exception of lead, it was found that in each case a certain thickness of filter existed at which the intensity of the forward transmitted secondary X-radiation was a maximum, an effect that has been observed by others for supervoltage X-rays (2). In the case of lead (Fig. 3d), it is doubtful whether the filter thickness yielding maximum intensity of secondary radiation was reached. Thinner lead foils with which to check this possibility were unavailable owing to war conditions. It may be observed that in each case the intensity of the secondary radiation reaching the receiver increases with increasing X-ray tube kilovoltage, and that for each of the three lighter metals the mass per unit area of filter required to give the secondary X-ray intensity maximum is relatively independent of the applied X-ray tube voltage for the voltage range considered. The secondary X-ray maxima were found to occur at 0.70, 0.04, and 0.07 gm. per cm.² mass per unit area for aluminium, copper, and tin respectively, and for lead the corresponding mass per unit area is known to be less than 0.02 gm. per cm.²

The quality of the secondary radiation from the various filters was examined in runs of Type (b). Observations were made for tin, copper, and aluminium. For tin and copper it was found that the effective absorption coefficients were considerably larger for small thicknesses of absorbing aluminium foils than for larger. Mass absorption coefficients fell from 1.7 cm.² per gm. for tin and 12 cm.² per gm. for copper to the common value of approximately 0.9 cm.² per gm. as the thickness of the absorber increased. The wave-lengths associated with these figures indicate that in each case the secondary radiation consisted of a combination of the K-fluorescence radiation of the filter material

plus a component of scattered radiation of effective wave-length corresponding to that of the primary X-ray beam. The ionizing power of the two components is approximately equally divided between the two types of radiation



FIGS. 3a TO 3d. Curves illustrating trend of experimental observations relating I_s (arbitrary units) to mass per unit area M (gm. cm.⁻²) of filter for runs of Type IV using aluminium, copper, tin, and lead filters respectively. Curves A, B, and C were obtained in each case using X-ray tube voltages of 115, 100, 85 kVp. respectively with X-ray tube current held constant for each filter.

for both metals. The secondary radiation from aluminium proved to be more nearly homogeneous than that from tin and copper, with the same effective absorption coefficient as that obtained for these two metals with thick layers of aluminium absorber, namely, $0.9 \text{ cm.}^2 \text{ per gm.}$ The absence of more precise numerical values of effective absorption coefficients in this section of the experiment arises from the difficulty of accurately comparing, with the apparatus available, intensities of X-rays having different wave-length ranges.

In Type (c) runs, a measure of the relative intensities of primary and forward transmitted secondary radiation emerging from an aluminium filter F placed at a distance of 20 cm. from the ionization chamber was obtained. The corrected rate of electrometer needle deflection caused by secondary X-rays entering the ionization chamber was measured using the procedure already described, and will be designated as R_1 . A set of rotating sectorized disks (8) were then inserted between B and the X-ray source S , and the ionization chamber was shifted upwards sufficiently to allow the same beam of primary X-rays transmitted by F to pass through the ionization chamber window, following which the rate of deflection R_2 due to primary plus secondary X-rays was measured. The intensity of the primary plus secondary beam was reduced to a known fraction f of its full value by means of the sectorized disks, so that R_1 and R_2 were of the same order of magnitude. If A_1 is the area of the window through which the secondary radiation reaches the ionization chamber, and A_2 the cross-sectional area of the primary beam as it enters the ionization chamber, the ratio I_s/I_p of the intensities of primary and secondary radiation entering the ionization chamber is given by the relation:

$$\frac{I_s}{I_p} = \frac{R_1 A_2}{R_2 A_1} f,$$

assuming that I_s is small compared to I_p .

For the aluminium filter tested under the above conditions, and with the X-ray tube operating at 100 kvp., a value of $\frac{I_s}{I_p} = 0.00029$ was obtained, which is found to increase to 0.15 at a distance of 1.0 cm. from the ionization chamber. Aluminium was chosen as the filter material in this measurement since it has been already observed that its secondary radiation has virtually the same effective wave-length as that of the primary X-ray beam, and hence difficulties arising out of a comparison of intensities where different wave-lengths are involved do not complicate the calculation. Similar runs were made with the other three metals, and it was found that under similar experimental conditions the ratio of secondary to primary intensities was of the same order of magnitude for each of these metals as for aluminium, although the heterogeneous secondary radiations obtained do not permit the statement here of significant numerical figures. In each case, filter masses per unit area that were found earlier to give the maximum intensity of secondary X-rays were used.

Results for runs of Type (d) for aluminium, copper, tin, and lead filters are presented in Figs. 4a and 4b, respectively. These are compared with the

theoretical predictions made by Seemann, which are shown as full straight lines in each figure. It is observed that within broad limits substantial agreement exists between measured and predicted X-ray intensities for all the metals studied, with perhaps a minor exception in the case of lead. For practical purposes the point of main interest is well demonstrated: for all cases studied under actual operating conditions with X-rays, the lowest possible intensity of X-rays at the receiver is obtained when the filter is placed as close as possible to the source for Arrangement I, and when $D_r = \frac{A}{2}$ for Arrangement II.

Discussion

The existence of a maximum in each of the curves of Fig. 3 is to be expected on theoretical grounds, since a relation has been obtained and compared with experiment for scattered radiation alone (2); and it can be shown that a relation of the same form holds when only fluorescence radiation is considered. Were one of the objects of this paper an experimental study of the above predictions, it would be necessary to insure that the primary X-ray beam used be monochromatic, and that the relative intensities and wave-lengths of the fluorescence and scattered X-radiation be known. The purpose of this paper is rather to supply usable experimental information on the distribution of secondary X-ray intensities from commonly used filter materials under those geometrical conditions most generally used, and with a beam of primary X-rays having a spectral distribution of intensity corresponding to that used as a standard*. Hence attention is directed at present only toward attaining these working conditions with the equipment available.

With reference to Type (d) runs in particular, differences between predicted and observed results do not appear to be caused by employment of the rate of deflection method for comparison of intensities, although this method has been held by Richtmyer (5) to be unreliable when several-fold differences in intensity magnitude are compared. That our measurements are reliable in this respect was checked by reducing the intensity of the beam of primary X-rays by known amounts with the set of rotating sectored lead disks, and observing the degree of direct proportionality between intensity of primary radiation incident on a given filter and the corresponding rates of deflection of the electrometer needle. A coefficient of linear correlation of $+0.99$ was observed between these two variables for rates of deflection of the same order of magnitude as were used throughout the present study, indicating that our measurements are not subject to Richtmyer's criticism to any significant degree.

It has been observed in this study that the value of $\frac{I_s}{I_p}$ for a single-metal filter can be minimized by the proper placement of filter relative to source, receiver, and defining apertures, and by the avoidance of use of filters having

* Radiologists use an X-ray tube current of 5.0 ma. at 100 kvp. as a standard reference setting. The X-ray tubes employed by most medical units have tungsten anticathodes. Taylor, Singer, and Stoneburner (7) find that X-ray qualities at a given effective voltage are nearly the same for all generators.

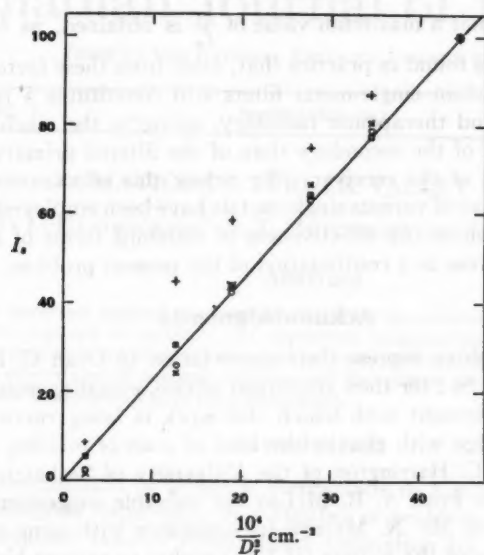


FIG. 4a

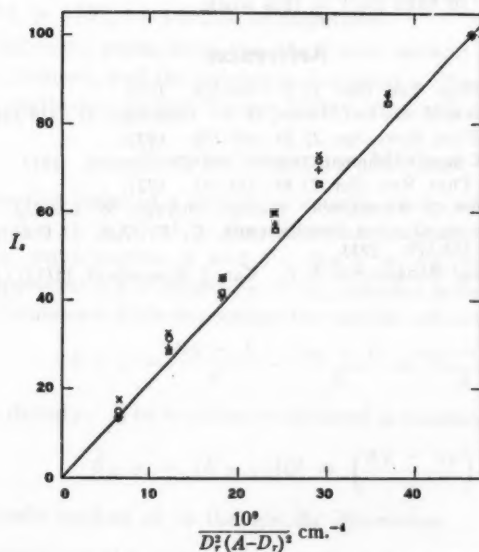


FIG. 4b

FIGS. 4a AND 4b. Results for runs of Type (d), Arrangements I and II respectively. Seemann's analysis predicts that $I_s = \frac{K_2}{D_f^2}$ for Arrangement I, and that $I_s = \frac{K'}{D_f^2 (A - D_f)^2}$ for Arrangement II (represented as a full line in each graph). Experimental points for aluminium, copper, tin, and lead are identified by the symbols: X, O, □, +, respectively.

thicknesses such that a maximum value of $\frac{I_s}{I_p}$ is obtained, as found in runs of Type (a). It is found in practice that, aside from these factors, secondary radiation from certain single-metal filters still constitutes a real hindrance in photographic and therapeutic radiology, owing to the much higher space rate of absorption of the secondary than of the filtered primary radiation in the surface layers of the receiver. To reduce this effect, compound filters composed of laminae of various single metals have been employed. An experimental examination of the effectiveness of standard forms of such filters is at present in progress as a continuation of the present problem.

Acknowledgments

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AROMATICS IN TURNER VALLEY CRUDES¹

By L. HENDRICKSON², A. T. HUTCHEON³, AND J. W. T. SPINKS⁴

Abstract

A dispersion method has been developed for the determination of aromatics in the presence of paraffinic and naphthenic hydrocarbons. The method has been applied to selected cuts obtained by fractionation of Turner Valley crudes. The percentages of benzene, toluene, and the xylenes occurring in a series of Turner Valley crudes have been determined.

Introduction

The determination of aromatic compounds in a mixture of hydrocarbons is of considerable importance in a number of problems. The methods commonly employed involve either direct estimation by means of a chemical reaction such as sulphonation or nitration (3, 8), or estimation by means of some physical property such as density (5, 17), aniline point (18), refractivity (2, 7, 10, 11, p. 1737, 13, 14, 20), or dispersion.

In the following paragraphs the dispersion method for the determination of benzene, toluene, and the xylenes is described. The results of the application of the method to certain Turner Valley crude oils are presented.

Specific Dispersion Method

The refractive index of a substance usually varies with wave-length. The dispersion, Δ_{X-Y} , is equal to the difference between the refractive indices for light of wave-lengths X and Y . $\Delta_{X-Y} = n_X - n_Y$. Similarly, the specific dispersion, δ'_{X-Y} equals $r_X - r_Y$, where r is the specific refractivity. Using the Gladstone-Dale expression for specific refractivity,

$$\delta'_{X-Y} = \frac{n_X - 1}{d} - \frac{n_Y - 1}{d} = \frac{n_X - n_Y}{d},$$

where d = density. The number so obtained is commonly multiplied by 10^4 , so that

$$\delta_{X-Y} = (\delta'_{X-Y})10^4 = \left(\frac{n_X - n_Y}{d}\right)10^4.$$

δ_{X-Y} is loosely spoken of as the specific dispersion. The Lorentz-Lorenz

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formula for specific refractivity, $\frac{n_x^2 - 1}{n_x^2 + 2} \cdot \frac{1}{d}$, may be used, but in most of the work described in the literature, the simpler Gladstone-Dale expression is employed. The densities are usually determined at 20° C. and referred to water at 4° C., i.e., d_4^{20} . The refractive indices are commonly determined at 20° C. for one or other of two pairs of lines, either the *F* and *C* hydrogen lines (4861 and 6563 Å), or the *g* and *e* mercury lines (4358 and 5461 Å respectively). The specific dispersions so obtained (multiplied by 10⁴) are δ_{F-C}^{20} and δ_{g-e}^{20} , respectively, e.g., $\delta_{g-e}^{20} = \frac{n_g^{20} - n_e^{20}}{d_4^{20}} \cdot 10^4$.

Dispersivity is pre-eminently a constitutive property and is said to be much more sensitive to structural differences than refractivity (1, 4). Ward and Kurtz (20) have collected and classified a great mass of data on the properties of hydrocarbons and have plotted δ_{F-C}^{20} against boiling point for each of the main classes of hydrocarbons. On inspection of their curves, some striking regularities are apparent: (a) the paraffins and naphthenes have a constant specific dispersion of 99, irrespective of boiling point; (b) the cyclic mono-olefines have a constant specific dispersion of 118; (c) the value for non-cyclic mono-olefines approaches that for the cyclic mono-olefines as the boiling point increases; (d) for the aromatics, specific dispersion is much higher than for the paraffins and naphthenes, and decreases with substitution in the benzene ring.

The method for determining aromatics in hydrocarbon mixtures by dispersion measurements is based on conclusions which may be drawn from these curves. For instance, it is apparent that if a crude that is free from olefines is fractionated so that each cut contains only one of the aromatics, the fraction may be treated as a mixture of two components. One component will be the aromatic and the other will be a mixture of the naphthenes and paraffins. The mixture of naphthenes and paraffins may be treated as a single component since members of these two hydrocarbon classes have nearly the same specific dispersion, irrespective of molecular weight or boiling point.

MacFarlane and Wright (16) have found that refractivity follows the mixture rule very closely when compositions are calculated on a volume basis. Small deviations are observed when compositions are calculated on a weight or mole basis. Specific dispersion also follows the mixture rule.

The first serious attempt to utilize specific dispersions for hydrocarbon analysis was made by Darmois in 1920 (6). Since then, Ward and Fulweiler (19), Fuchs and Anderson (10), Ward and Kurtz (20), and Grosse and Wackher (12) have furthered the development and enlarged the field of utility of the method. The present method follows that of Grosse and Wackher rather closely but differs in that the mercury lamp, instead of a hydrogen tube, is used as light source.

Experimental

Measurement of Dispersion

The Pulfrich refractometer with temperature control was used to determine the dispersion at 20° C. for the *e* and *g* lines from a mercury vapour lamp. The *e* and *g* lines from an ordinary mercury vapour lamp are usually much more intense than the *F* and *C* lines from a hydrogen tube, and this is a factor of some importance when many dispersions have to be measured. The dispersion can be measured rapidly and the resulting specific dispersion should have an accuracy of 0.1 to 0.2 units.

Alternatively, the Abbé refractometer may be used to determine dispersions but the accuracy obtainable is only about one-tenth that obtainable with a Pulfrich refractometer. Fuchs and Anderson (10) describe a dispersometer that is said to be more easily manipulated than the Pulfrich and achieves an accuracy of one dispersion unit.

Measurement of Density

The relative density, d_{20}^{20} , can be measured with a sufficient degree of accuracy using a Mohr-Westphal balance (9). Where only small quantities of liquid are available a pycnometer may be used.

Verification of Method

Known series were made up, on a weight percentage basis, in which an aromatic was mixed with a paraffin of approximately the same boiling point range. The series were made up of

- Mixtures of benzene and hexane,
- Mixtures of toluene and 2,2,4-trimethyl pentane,
- Mixtures of 2,2,4-trimethyl pentane with a mixture of the isomeric xylenes.

Data for the series are recorded graphically in Fig. 1. Data concerning the materials are given in Table I. It is seen that, in agreement with the results of other workers, the weight percentage composition is a linear function of the specific dispersion. With care and some practice, compositions can be determined to $\pm 1\%$ using specific dispersions.

TABLE I
MATERIALS

| Material | Maker | Grade | d_{20}^{20} | | n_D^{20} | |
|-------------------------|---------|----------|---------------|------------|------------|------------|
| | | | Actual | Literature | Actual | Literature |
| Benzene | Merck | Reagent | 0.8779 | 0.8789 | 1.50067 | 1.50165 |
| Toluene | Merck | Purified | .8643 | .8669 | 1.49578 | 1.49552 |
| Xylene | Merck | Reagent | .8656 | | 1.49775 | |
| Hexane | Eastman | Pract. | .6621 | .6595 | 1.37567 | 1.37515 |
| 2,2,4-Trimethyl pentane | Eastman | Tech. | .6947 | .6918 | 1.39331 | 1.39162 |

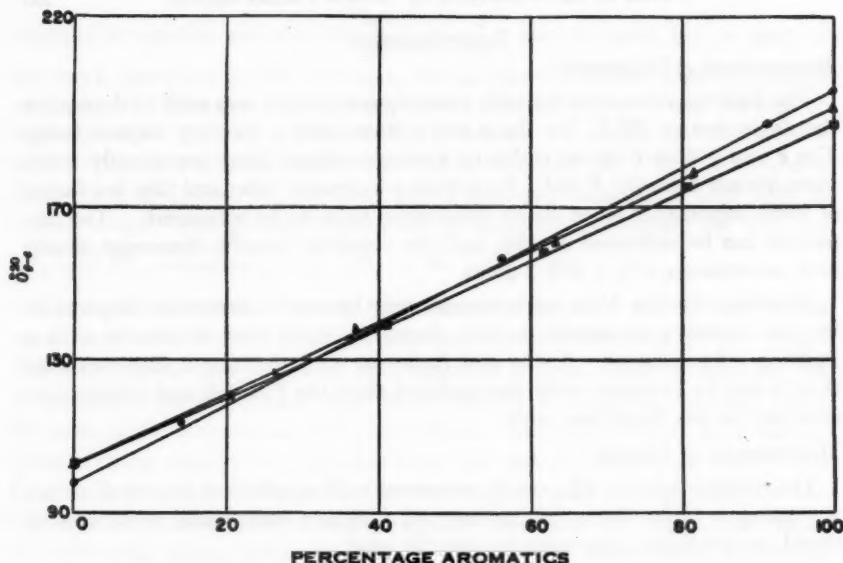


FIG. 1. δ_{p-s}^{20} vs. percentage aromatics: \circ , benzene and hexane; \triangle , toluene and 2,2,4-trimethyl pentane; \square , xylene and 2,2,4-trimethyl pentane.

Application to Turner Valley Crudes

Previous work (7, 21) has shown that when Turner Valley crudes are fractionated in Stedman columns, the cut from 60 to 90° C. will contain all the benzene, the cut from 90 to 120° C. all the toluene, and the cut from 120 to 150° C. all the xylenes. The crudes do not contain unsaturates and thus no allowance need be made for them (unsaturates can be allowed for by determination of the bromine number (12)).

The dispersions of the hydrocarbons vary slightly with boiling point and it is therefore necessary, in accurate work, to determine so-called base values for the different cuts. The base value is the specific dispersion for the hydrocarbons, other than aromatics, present in the cut. For example, the xylene cut from crude oil from Foundation 1 well, after removal of aromatics by nitration, gave the following data: $d_4^{20} = 0.7236$, $n_D^{20} = 1.41209$, $n_D^{20} = 1.40480$, whence $\delta_{p-s}^{20} = 100.7$.

As a result of numerous determinations, the following base values are suggested: for the benzene cut, 97.3; for the toluene cut, 99.1; for the xylene cut, 100.5. The specific dispersions, δ_{p-s}^{20} for benzene, toluene, and xylene were found to be 201.2, 196.3, and 192.0 respectively (for details of measurements see thesis by L. Hendrickson, University of Saskatchewan, 1941). Using these values and the appropriate base value, the following formulae are

easily derived (based on a linear relation between specific dispersion and weight per cent composition, W):

$$\text{Benzene cut: } \delta_{D-e}^{20} = 97.3 + 1.039 W.$$

$$\text{Toluene cut: } \delta_{D-e}^{20} = 99.1 + 0.972 W.$$

$$\text{Xylene cut: } \delta_{D-e}^{20} = 100.5 + 0.915 W.$$

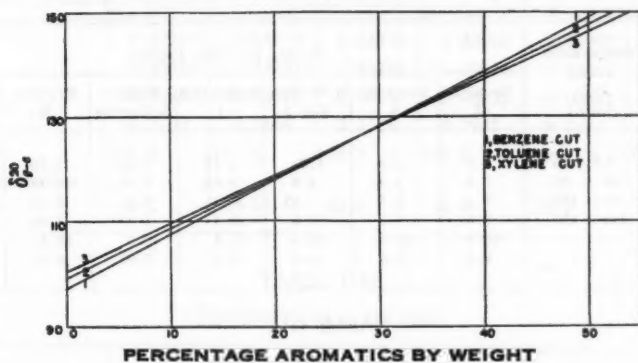


FIG. 2. δ_{D-e}^{20} vs. percentage aromatics for cuts from Turner Valley crudes.

These relations are represented graphically in Fig. 2. It should be remembered that this figure applies to cuts from Turner Valley crudes from the paleozoic limestones and to dispersions determined for the g and e mercury lines.

The curves have been checked by measurements of dispersion on samples made up by weight; for example, from reagent toluene plus the toluene cut freed from aromatics by nitration. They have also been checked by determinations of aromatics in numerous samples by nitration as well as by dispersion (see, for example, Table IV).

Formulae giving the percentages of aromatics are:

$$60 \text{ to } 90^\circ \text{ C. cut: wt. \% benzene} = 0.962 \delta_{D-e}^{20} - 93.6$$

$$90 \text{ to } 120^\circ \text{ C. cut: wt. \% toluene} = 1.029 \delta_{D-e}^{20} - 102.0$$

$$120 \text{ to } 150^\circ \text{ C. cut: wt. \% xylenes} = 1.093 \delta_{D-e}^{20} - 109.8$$

The value for the xylenes will be approximate only since a mixture, containing 92% *m*-xylene, was used in determining the curve for xylene, and there is no assurance that the isomers will be present in the same proportions in the cut as in the calibrating mixture. However, the error should not be serious since the specific dispersions of *o*-, *m*-, and *p*-xylene lie within 1% of one another (see, for example (12)).

Procedure

A 1000 cc. sample of crude oil was fractionated in a 3 ft. Stedman column (21) 1 in. in diameter. The ratio of reflux to product was 15 : 1. Cuts were made at 60 to 90°, 90 to 120°, and 120 to 150° C. Determinations of the

density and dispersion of each cut were carried out; from these the specific dispersion could be calculated and the percentage aromatics determined.

TABLE II

FRACTIONATION IN A 3 FT. STEDMAN COLUMN, 1 IN. IN DIAMETER

Charge: 1000 cc. at 24° C. Barometer, 720 mm. Ratio reflux: product = 15 : 1

| Sample No. | Temperature range, °C. (corr.) | Volume per cent distilled | | | | | | |
|------------|--------------------------------|---------------------------|-------------|-----------------|--------------|------------------|-------------|-------------|
| | | Royalite 45 | Foothills 6 | N.W. Hud. Bay 2 | Foundation 1 | Home-Millarville | Royalite 31 | Royalite 43 |
| 1 | I.B.P.—60 | 2.0 | 3.2 | 1.05 | 6.15 | 2.57 | 2.50 | 1.65 |
| 2 | 60 — 90 | 5.6 | 5.3 | 4.0 | 9.64 | 5.25 | 5.49 | 7.06 |
| 3 | 90 — 120 | 9.1 | 8.3 | 7.85 | 13.34 | 7.80 | 8.40 | 7.86 |
| 4 | 120 — 150 | 7.6 | 7.1 | 8.6 | 10.3 | 6.47 | 7.66 | 6.20 |
| Residue | | 66.4 | 69.5 | 72.1 | 51.5 | 70.0 | 69.8 | 70.0 |
| Loss | | 9.3 | 6.6 | 6.4 | 9.1 | 7.91 | 6.15 | 7.23 |

TABLE IIIa

DISPERSION DATA ON CUTS

| Sample No. | Royalite 45 | | | Foothills 6 | | |
|---------------------------|-------------|---------|---------|-------------|---------|---------|
| | 2 | 3 | 4 | 2 | 3 | 4 |
| n_D^{20} | 1.40664 | 1.42791 | 1.44633 | 1.40543 | 1.42864 | 1.44824 |
| n_g^{20} | 1.39902 | 1.41917 | 1.43045 | 1.39777 | 1.41987 | 1.43824 |
| $n_D^{20} - n_g^{20}$ | 0.00762 | 0.00874 | 0.00988 | 0.00766 | 0.00877 | 0.0100 |
| d_4^{20} | 0.7069 | 0.7442 | 0.7725 | 0.7036 | 0.7477 | 0.7728 |
| δ_{p-s}^{20} | 107.8 | 117.5 | 128 | 108.9 | 117.2 | 129.3 |
| Per cent aromatics in cut | 9.7 | 18.5 | 30.0 | 10.8 | 18.5 | 31.5 |

TABLE IIIb

DISPERSION DATA ON CUTS

| Sample No. | N.W. Hudson's Bay 2 | | | Foundation 1 | |
|---------------------------|---------------------|---------|---------|--------------|---------|
| | 2 | 3 | 4 | 2 | 3 |
| n_D^{20} | 1.40802 | 1.42990 | 1.44536 | 1.40391 | 1.42616 |
| n_g^{20} | 1.40036 | 1.42103 | 1.43563 | 1.39643 | 1.41760 |
| $n_D^{20} - n_g^{20}$ | 0.00766 | 0.00885 | 0.00973 | 0.00748 | 0.00856 |
| d_4^{20} | 0.7119 | 0.7505 | 0.7728 | 0.7038 | 0.7433 |
| δ_{p-s}^{20} | 107.6 | 117.9 | 126 | 106.3 | 115.2 |
| Per cent aromatics in cut | 9.7 | 19.0 | 27.8 | 7.0 | 16.5 |

TABLE IIIc
DISPERSION DATA ON CUTS

| Sample No. | Royalite 31 | | | Royalite 43 | | |
|---------------------------|-------------|---------|---------|-------------|---------|---------|
| | 2 | 3 | 4 | 2 | 3 | 4 |
| n_D^{20} | 1.40765 | 1.43015 | 1.44743 | 1.40590 | 1.43207 | 1.44918 |
| n_D^{30} | 1.40014 | 1.42137 | 1.43776 | 1.39854 | 1.42316 | 1.43934 |
| $n_D^{30} - n_D^{20}$ | 0.00751 | 0.00878 | 0.00967 | 0.00736 | 0.00891 | 0.00984 |
| d_4^{20} | 0.7100 | 0.7468 | 0.7720 | 0.7037 | 0.7483 | 0.7733 |
| δ_{D-4}^{20} | 105.8 | 117.6 | 125.2 | 104.5 | 119.1 | 127.3 |
| Per cent aromatics in cut | 8.1 | 18.85 | 26.7 | 6.9 | 20.5 | 29.1 |

TABLE IIIId
DISPERSION DATA ON CUTS

| Sample No. | Home Millarville 2 | | | |
|---------------------------|--------------------|---------|---------|---------|
| | 2 | 3A* | 3B* | 4 |
| n_D^{20} | 1.40802 | 1.42384 | 1.44333 | 1.44508 |
| n_D^{30} | 1.40045 | 1.41556 | 1.43333 | 1.43528 |
| $n_D^{30} - n_D^{20}$ | 0.00757 | 0.00828 | 0.01000 | 0.00980 |
| d_4^{20} | 0.7107 | 0.7381 | 0.7657 | 0.7688 |
| δ_{D-4}^{20} | 106.7 | 112.1 | 130.6 | 127.5 |
| Per cent aromatics in cut | 9.0 | 13.3 | 32.2 | 29.5 |

* Cut 3 in two parts: 3A, 88 to 103° C., 5% } 7.8% (See Table II)
3B, 103 to 119° C., 2.8%

The percentage aromatics in a large number of samples was checked by nitration (3). The agreement obtained was good and is illustrated by a few results obtained on the toluene cuts (see Table IV). The nitrations were

TABLE IV
PERCENT TOLUENE (BY WT.) IN CUT

| | Home-Millarville 2 | Royalite 31 | Royalite 43 |
|------------|--------------------|-------------|-------------|
| Dispersion | 13.3 | 18.8 | 20.5 |
| Nitration | 12.9 | 18.84 | 20.26 |

run in duplicate. The percentage aromatics in a given cut being known, that in the crude can be calculated.

Example. Foundation 1: Percentage toluene in cut 3 = 16.5. Density of cut = 0.7433. Volume of cut expressed as percentage of crude = 13.34. Density of crude oil = 0.7936. Percentage toluene by wt. in crude = $\frac{13.34 \times 16.5 \times 0.7433 \times 10}{793.6} = 2.05$.

The results are summarized in Table V, which shows the location and depth of the well, together with the A. P. I. gravity of the crude.

TABLE V
ESTIMATE OF AROMATICS IN TURNER VALLEY CRUDES

| Well | Location | Depth, ft. | A.P.I. at 60° F. | Per cent by wt. in crude oil | | |
|-----------------------|---------------------|---------------|------------------------|------------------------------|---------|-------------------------------|
| | | | | Benzene | Toluene | Xylenes + ethyl benzene |
| North Turner Valley | | | | | | |
| Home-M. 2 | 6 of 33, 20-3, W-5 | 8495 | 40.4 | 0.41 | 1.44 | 1.79 |
| Foothills 6 | 5 of 27, 20-3, W-5 | 8140 | 41.9 | 0.49 | 1.34 | 2.1 |
| Royalite 43 | 2 of 22, 20-3, W-5 | 8800 | 41.1 | 0.42 | 1.48 | 1.71 |
| Central Turner Valley | | | | | | |
| Royalite 45 | 14 of 5, 19-2, W-5 | 7486 | 44.1 | 0.48 | 1.52 | 2.2 |
| South Turner Valley | | | | | | |
| Sterl. Pac. 3* | 14 of 33, 18-2, W-5 | 6788 | 45.8 | 0.35 | 2.18 | 2.71 |
| Royalite 31 | 6 of 29, 18-2, W-5 | 8064 | 39.4 | 0.38 | 1.44 | 1.92 |
| Foundation 1 | 5 of 21, 18-2, W-5 | 6474 | 46.8 | 0.63 | 2.05 | |
| N.W.H. Bay 2 | 9 of 8, 18-2, W-5 | 7591 | 39.0 | 0.33 | 1.30 | 2.2 |

* Taken from Donald (7).

The wells investigated give a reasonable cross-section of the Turney Valley field, and, as far as can be seen, there is no relation between aromatic content and position in the field. However, it can be stated in a general way that the lighter the crude, the greater the percentage of toluene. A comparison with crudes from other fields is difficult. As is well known, certain Borneo crudes are very high in aromatics but North American oils are usually relatively poor in aromatics, e.g., one well in the Oklahoma field contains 0.3% toluene (15).

Acknowledgments

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STUDIES IN URETHANES

VII. REACTIONS OF ACYL DIURETHANES WITH AMMONIA AND PRIMARY AMINES. STABILIZING EFFECT OF THE PHENYL RADICAL IN PHENYLMALONYL- AND PHENYLSUCCINYLDIURETHANE¹BY S. BASTERFIELD² AND A. J. DYCK³

Abstract

In previous studies it has been shown that the mechanism of decomposition of acyl diurethanes by ammonia and amines is correlated to some extent with the strength of the acid from which the acyl radical is derived and of the base used as ammonolytic reagent. In the oxalic acid series a diurea was obtained from succinyl-diurethane and aniline, but not from oxalyl- or malonyl-diurethane. Succinyl-diurethane gave no diurea with stronger bases.

It is shown in the present study that phenylmalonyl-diurethane yields with aniline a diurea which undergoes rapid decomposition on being heated with aniline at 150° C. Phenylsuccinyl-diurethane gives with aniline a diurea that is much more stable than the one obtained from succinyl-diurethane, as judged by the rate of decomposition on heating with aniline at 150°. No definite evidence of diurea formation was obtained with bases stronger than aniline.

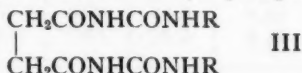
In previous studies on the reactions of acyl diurethanes with ammonia and amines (2, 3), it has been shown that:

- (a) Oxalyl-, malonyl-, and phthalyl-diurethanes are decomposed with the loss of one or both urethane (carbethoxy-amino) groups and the formation of amides of the dibasic acids, or of urethano- and ureido-amides (I, II)



without the appearance of acyl diureas;

- (b) Succinyl-, glutaryl-, and adipyl-diurethanes yield, with ammonia and ethylamine, amides, but with aniline, acyl diphenylureas (III)



which are decomposed by further action of the base into anilides of the dibasic acids and diphenylurea. It was pointed out that the tendency of diurethanes to lose urethane groups and give amides rather than diureas is correlated in some measure with the strength of the acid from which the acyl radical is derived and that of the base used as ammonolytic reagent.

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As a further contribution to this problem an examination has been made of the effect on the course of the reactions of introducing a phenyl radical into the acyl groups of malonyl- and succinyl-diurethane. The influence of the phenyl radical on the ionization constants of malonic and succinic acids is shown in Table I. The value in both instances is considerably more than doubled. Since malonyl-diurethane with aniline gave no evidence of diurea formation while succinyl-diurethane yielded a diurea, it might be expected, considering the factor of acid strength alone, that phenylmalonyl-diurethane would not yield a diurea while phenylsuccinyl-diurethane might or might not do so, seeing that the ionization constant of phenylsuccinic acid lies between that of malonic acid and that of succinic acid in the region 10^{-4} .

TABLE I
TABLE OF IONIZATION CONSTANTS

| Acid | K |
|----------------|---------------------------|
| Malonic | 1.23×10^{-3} |
| Phenylmalonic | 2.77×10^{-3} (1) |
| Succinic | 6.6×10^{-3} |
| Phenylsuccinic | 1.58×10^{-4} |

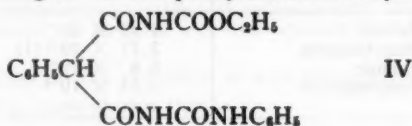
The presence of a phenyl radical, however, intrudes another factor into the situation. The stabilizing effect of the phenyl radical on relatively unstable molecules has long been recognized, and has been attributed in recent physico-chemical theory to the resonant property of the benzene ring. This effect would tend to offset the influence of the first factor, and the formation and persistence of a diurea might well depend on which influence was dominant. Furthermore if a diurea were formed from phenylsuccinyl-diurethane its stability might readily be compared with that of succinyl-di-(phenylurea).

Experiment showed that the stabilizing influence of the phenyl radical was operative, since both phenylmalonyl- and phenylsuccinyl-diurethane gave diureas during two hours' heating with aniline, the first at 150°C . and the second at 180°C . Phenylsuccinyl-di-(phenylurea) is unquestionably more stable than succinyl-di-(phenylurea), as shown by its rate of decomposition with aniline. The succinyl compound was obtained after one hour's heating of the diurethane with aniline, and it disappeared entirely during a second hour's heating at the same temperature. The phenylsuccinyl compound was obtained in good yield after two hours' heating of the diurethane at 180° , and the diurea was still present in considerable amount after a third hour of heating at 180° to 200° . Even allowing for a difference in the rates of formation of the diureas, it seems safe to conclude that the phenylsuccinyl-diurea is the more stable.

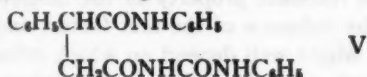
Phenylmalonyl-di-(phenylurea) has a stability much closer to that of succinyl-di-(phenylurea), though it is difficult to make an accurate comparison. The succinyl compound was formed and decomposed during two hours'

heating at 150° C., while the phenylmalonyl compound was isolated after two hours' heating, together with phenylmalonanilide (28%) and diphenylurea, indicating that some decomposition of the diurea had taken place. It is true that each diurea was completely decomposed during one hour's heating at 150°, and this suggests about equal stability for the two compounds. The fact, however, that in the original preparation of the phenylmalonyl compound there was undecomposed diurea still present after two hours' heating suggests that perhaps it is somewhat more stable than succinyldi-(phenylurea). This would be more certain if the rates of formation of the two diureas were of the same order, a not unreasonable assumption, though no data on this point have been obtained.

From the reaction of phenylmalonyl-diurethane with aniline at 150° C. a small quantity of another product was obtained. Its identity was not established satisfactorily by analysis, but because of its relatively low melting point, 151° C.*, it was regarded as impure phenylureido-phenylmalonyl-urethane (IV) analogous to the phenylureido-succinylurethane, m.p. 163°,



obtained in an earlier study (2), rather than phenylureido-phenylmalonanilide. Such a ureido-anilide was obtained, however, from phenylsuccinyl-diurethane (V)†. It melted at 234° and was isolated from the reaction mixture after three hours' heating at 180° to 200°.



It probably represents a stage in the decomposition of the acyldi-(phenylurea) to the acyldi-anilide.

It should be noted that considerable difficulty was experienced in obtaining some of the products of the above reactions reasonably pure. The diureas, anilides, and intermediate products often required tedious recrystallization to free them from related compounds. The melting points of the diureas, of phenylureido-phenylsuccinanilide and of diphenylurea all lie within the range 234° to 237°.‡ Since diphenylurea was a constant product of prolonged reaction with aniline it was necessary to establish its identity repeatedly by a mixed melting point determination with a known sample.

One experiment was made on the decomposition of malonyl-diurethane with aqueous cyclohexylamine (30%). A good deal of gummy material was obtained but from it were isolated malon-dicyclohexyl-amide and urethane. This base thus resembled ethylamine in its action.

* All melting points are uncorrected.

† Cf. also malonyl-diurethane (3).

‡ Cf. phenylureido-malonanilide (3).

Experimental

Preparation of Acyl Diurethanes

Phenylmalonyl-diurethane, $C_6H_5CH \cdot (CONHCOOC_2H_5)_2$. This compound was prepared, as described in a previous paper (2), from phenylmalonic acid, phosphorus oxychloride, and urethane; m.p., 154° C. Yield, about 25%.

Phenylsuccinyl-diurethane, $C_6H_5CH \cdot CH_2(CONHCOOC_2H_5)_2$. Phenylsuccinic acid, urethane, and phosphorus oxychloride in suitable proportions were mixed together and allowed to stand at room temperature for several days. The temperature was then raised to 40° C. for six hours, and finally to 50° for two to three hours. The semisolid mass was left in contact with water overnight, and the white solid obtained recrystallized from alcohol; m.p., 162° C. Yield, about 15%. Calc. for $C_{16}H_{18}N_2O_6$: N, 8.38%. Found: N, 8.42, 8.47%. In this preparation, considerable blackening of the reaction mixture occurs if the temperature is raised only moderately immediately after the reactants are mixed. The procedure outlined above gave the best results although the yield was disappointing.

Reactions of Phenylmalonyl-diurethane

With ammonia. Three grams of the diurethane was mixed with 25% aqueous ammonia and allowed to stand for a week at room temperature. A white precipitate formed. It was identified as phenylmalonamide, previously prepared by Dox and Yoder (4); m.p., 232° C. Calc. for $C_9H_{10}N_2O_2$: N, 15.73%. Found: N, 15.50, 15.50%. The ammoniacal filtrate was evaporated at 50° and the residue extracted with ether. The ether extract yielded urethane. The ether insoluble residue (0.2 gm.) decomposed at 270° to 280°. It contained 18% of nitrogen, and was probably impure ammonium phenylbarbiturate (N, 19%). Ammonium barbiturate is formed in the analogous reaction with malonyl-diurethane (3).

With Ethylamine. Three grams of the diurethane was treated with 25% aqueous ethylamine for a week at room temperature. Large branching crystals separated; m.p. 154° C. It was apparently phenylmalon-diethylamide. Yield, 60%. Calc. for $C_{13}H_{18}N_2O_2$: N, 11.96%. Found: N, 11.67%. The filtrate was evaporated and the residue extracted with ether and alcohol. The extract yielded urethane. The small insoluble residue was not absolutely identified, but it was probably the impure ethylamine salt of phenylbarbituric acid (see preceding section). Calc. for $C_{12}H_{16}N_2O_3$: N, 16.8%. Found: N, 16.3%.

With Aniline (at 150° C.). Two grams of diurethane was heated with 9.5 gm. of aniline for two hours at 150° C. Fine crystals separated on cooling. Ether was added and the mixture filtered. The ether insoluble portion melted at 204° to 205°. It was undoubtedly phenylmalonanilide. The yield was 28%. Calc. for $C_{21}H_{18}N_2O_2$: N, 8.48%. Found: N, 8.27, 8.39%. The ethereal filtrate was evaporated until crystals appeared. The product was recrystallized from hot alcohol; m.p., 234° to 235°. It was apparently phenylmalonyldi-(phenylurea). Calc. for $C_{22}H_{20}N_4O_4$: N, 13.46%. Found:

N, 12.97, 12.89%. When this product was heated with aniline for one hour at 150° to 160° it was converted completely to phenylmalonanilide and diphenylurea.

The ether filtrate was completely evaporated to dryness. The residue was separated by fractional crystallization into diphenylurea (m.p. 236° C.) and a small quantity of substance melting at 151°. This was probably phenylureido-phenylmalonyl-urethane (IV)*. Calc. for $C_{19}H_{19}N_3O_3$: N, 11.38%. Found: N, 10.85, 10.94%.

With Aniline (at 180° to 190°). Two grams of the diurethane was heated with 9.5 gm. of aniline at 180° to 190° for two hours. The semisolid mass obtained was treated with ether and filtered. The crystalline product was identified as phenylmalonanilide. From the filtrate, diphenylurea was obtained. A small gummy residue was left but no other crystalline products were obtained.

Reactions of Phenylsuccinyl-diurethane

With Ammonia. Two grams of the diurethane was treated with 25% ammonia for a week at room temperature. The crystalline product that separated was identified as phenylsuccinamide. Calc. for $C_{10}H_{12}N_2O_2$: N, 14.58%. Found: N, 14.50%. The ammoniacal filtrate yielded urethane.

With Ethylamine. By a procedure similar to the above, using aqueous ethylamine, a 60% yield of phenylsuccinyl-diethylamide was obtained; m.p., 179° to 180°. Calc. for $C_{14}H_{17}N_2O_2$: N, 11.10%. Found: N, 11.42%. The filtrate yielded urethane.

With Aniline (1) at 180° C. The diurethane (1.5 gm.) and aniline (8 gm.) were heated for two hours at 180° C. The viscous mass was taken up in ether. A crystalline product was filtered off. It was washed with ether to remove gum and recrystallized from alcohol; m.p. 235°. It was apparently phenylsuccinyl-di-(phenylurea) and was the main product of the reaction. Calc. for $C_{24}H_{28}N_4O_4$: N, 13.02%. Found: N, 12.80, 12.86%. From the ether filtrate a small amount of diphenylurea was obtained; this indicated some splitting of urethane from the original compound. There was considerable formation of unresolvable gum.

With Aniline (2) at 180° to 200° C. One gram of the diurethane was heated with 5 gm. of aniline for three hours at 180° to 200°. Phenylsuccinyl-di-(phenylurea) was again obtained (0.3 gm.). The ether filtrate on evaporation yielded a small amount of flocculent material. This was recrystallized from alcohol. It melted at 234° but was not the diurea. It was apparently phenylureido-phenylsuccinanilide, a decomposition product of the diurea. Calc. for $C_{21}H_{21}N_3O_3$: N, 10.85%. Found: N, 11.00, 11.14%. From the final gummy residue, diphenylurea was obtained.

* Phenylureido-phenylmalonanilide has a nitrogen content of 11.26% but it is almost certain that this substance would have a much higher melting point, probably in the region of 230° to 235°. It was expected that this compound would be formed but no appreciable quantity was isolated.

Reaction of Malonyl-diurethane with Cyclohexylamine

Diurethane (2 gm.) was refluxed with 30% aqueous cyclohexylamine for a short time. A white crystalline substance separated when the solution cooled; m.p. 174° C. Yield, 0.64 gm. It was malon-di-cyclohexylamide. Calc. for $C_{15}H_{26}N_2O_2$: N, 10.52%. Found: N, 10.49, 10.52%. From the evaporated filtrate a gummy mass was obtained which yielded urethane by extraction with ether.

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THE ADEQUACY OF VITAMIN C IN ALBERTA DIETS¹

BY HILDA K. WAAGEN² AND L. B. PETT³

Abstract

A survey was carried on for 12 months to determine the amount of vitamin C actually available in the food served in Athabasca Hall, a residence for men at the University of Alberta. The amount of vitamin C excreted by some of the persons living at Athabasca Hall was also determined and correlated with the intake. It was found that the output was higher in the fall after high intake than in the spring after the low supply during the winter. The average daily intake of vitamin C from November to May, inclusive, was 41 mg., and from June to October, inclusive, 82 mg. If citrus fruits had been excluded from the diet, the intake would have been markedly less. In the spring months the tissues of all persons tested by a test dose method were found to be unsaturated, whereas in the autumn two persons out of six showed tissue saturation. No frank scurvy existed among the subjects and no marked incidence of gum-bleeding was reported.

Introduction

Attention has been focused by many investigators on determining whether the amount of vitamin C excreted in the urine has a fixed, definite relation to the vitamin C requirements of the body. It has been confirmed that the amount of ascorbic acid excreted in the urine is dependent on the degree of tissue saturation (9, 10, 16), which in turn is dependent on the previous diet. The quantity excreted varies so greatly even with the same individual that it is difficult to state in arbitrary figures a normal value for all people (9). Spellberg and Keeton (16), after a survey of the literature, placed the minimum normal amount excreted at 20 mg. in 24 hr. Harris *et al.* (8) noted that the normal daily output remained fairly constant at 30 to 33 mg., but in later work (1) they state 20 mg. per day to be the rate of excretion on a moderately low intake, and that 10 to 15 mg. per day represents the borderline group. However, Evelyn, Malloy, and Rosen (6) have found with the photoelectric colorimetric method that apparently normal healthy individuals have a 24 hr. output of 5 mg. or less. Thus there is some doubt in interpreting the rate of urinary output of vitamin C as an indication of dietary adequacy of the vitamin.

Many people consider that tissue saturation is better evidence of dietary adequacy of vitamin C. It is determined by titration of urine samples, before and after the administration of test doses. The percentage output of the dose in 24 hr. is low if the tissues are unsaturated, and if they are fully saturated, 60 to 80% will be excreted (2). Excretion of 50% or more of

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the test dose can be taken as an indication of tissue saturation (15). On the basis of these tests the daily requirement for vitamin C has been placed as high as 100 mg.

Although these determinations give some knowledge regarding the saturation of the tissues, it is doubtful whether saturation is necessary for optimal health. Rietschel and Mensching (13) experimented with a vitamin-C-free diet, on which one of them lived for 100 days without manifestation of prescorbutic symptoms. He appeared quite as healthy at the end of the test period as he had at the beginning, although the level of vitamin C in the blood and the amount excreted in the urine were virtually zero. These authors state that a daily intake of 15 mg. may be adequate.

It is apparent that the literature on vitamin C contains many differing results and opinions so that at the present time no agreement exists regarding the best method of determining vitamin C adequacy. In the past three years, the tendency has been to assume, without adequate clinical evidence, that tissue saturation is essential. The final solution of the problem demands further clinical work. However, most investigators agree that more than the minimum preventive dose should be taken daily.

This and similar questions regarding other vitamins can be finally answered only by studying groups of people on controlled intakes of the vitamin, determined by analyses. Much work remains to be done on these problems.

As described in this paper, the authors have determined in average figures the actual daily consumption of vitamin C by persons subsisting on an ordinary, well balanced diet. They also determined the output of the vitamin by some of these persons, in order to correlate the daily intake with the amount excreted. This work is of importance not only as the first of its kind in Western Canada, but also as a contribution to the general problem of human requirements for vitamin C.

Experimental

For one week in each of 12 months, from December, 1939, to December, 1940, the vitamin C contents of foods served in Athabasca Hall, a residence for male students of the University of Alberta, were determined. The kitchens supply food for approximately 400 students. When possible, all vegetables are cooked with steam; fruits are stewed. Thus, it was assumed that the meals served there would be fairly representative of better class or well supervised, large-scale selection and preparation of foods.

In summer, most of the vegetables were obtained fresh from the University gardens; in the winter, stored vegetables, such as potatoes, carrots, turnips, cabbage, etc., and canned vegetables, such as peas and beans, were used. The oranges, apples, grapefruit, and bananas were fresh or stored, depending on the season during which they were obtained. In the winter, any fruits other than the above mentioned were canned (peaches, pears, plums, pineapple), whereas in the summer other fresh fruits, such as peaches, plums, raspberries, and strawberries, were obtainable.

During the apple season, more of this fruit was served than any other. In the summer months of July, August, and September, apples were omitted, oranges being the main fruit; occasionally the latter were replaced by cherries, peaches or grapes.

The results are calculated on servings of the following amounts: vegetables and stewed fruits—100 gm.; oranges, apples, peaches—one fruit; grapefruit—one-half.

The ascorbic acid was estimated in any fresh fruit served at breakfast, and in the vegetables and fruits served at dinner and supper. It was not determined in meats as the amount of vitamin C contained in meat after cooking is considered to be negligible (14). Soups and milk were not tested (5 mg. of vitamin C in one pint of milk (3)).

The estimations were carried out during the first complete week of each month (Monday to Saturday). Actual determinations of ascorbic acid in the food served on Sunday were not made, but the amount was calculated from the values obtained on the preceding six days.

The procedure adopted was a modification of the 2,6-dichlorophenol-indophenol titration method (7). The extracting acid was a 2% solution of metaphosphoric acid in 2 *N* hydrochloric acid. This mixture had no appreciable effect on the dye; no decolorization took place until three or four minutes had elapsed. The dye solution was run from a 10 ml. microburette into 5 ml. of the hydrochloric-metaphosphoric acid extract of the tissue under examination. A pink colour that persisted for 10 sec. was taken as the end-point of the titration.

The preparation of the acid extract was similar to the methods used by Pett (12) and by Thornton (17). A sample, obtained by quartering, was weighed (20 gm.), immediately placed in a beaker, and covered with the acid mixture. It was then ground in a mortar, with sand if necessary, to a fairly fine pulp. The grinding was not prolonged beyond the minimum time necessary. The mixture was then poured into a graduated cylinder, the mortar and beaker were rinsed with acid solution, and the washings added to the contents of the cylinder. The final volume was made up to 80 ml. The mixture was allowed to stand a few minutes, with occasional shaking, and it was then filtered into a beaker containing a pinch of zinc dust. The zinc reacts with the hydrochloric acid and the hydrogen evolved reduces any dehydro-ascorbic acid to ascorbic acid. The zinc was allowed to react for three to five minutes, or until the foam subsided. When potatoes, or any creamed or very starchy vegetables are being tested, it is better to centrifuge the mixture in order to obtain a clear extract.

The McHenry and Graham (11) modified method for the titration of deeply coloured extracts was used when necessary.

The indophenol dye solution was standardized against a solution of known ascorbic acid content. The phosphate buffer (pH 7.2) used in preparation of the dye solution stabilized it sufficiently that restandardization was neces-

sary only every two weeks. The strength was such that 1 cc. was approximately equivalent to 0.200 mg. of ascorbic acid.

Reduction of dehydro-ascorbic acid was effected by means of zinc in preference to hydrogen sulphide (5, 4), as it is the more rapid procedure. It is possible that zinc will reduce other substances so that they will also reduce the dye. Experiments with raw potato extract showed that three to five minutes was sufficient time for the reduction by zinc.

The method was further tested for reliability and was found to be satisfactory. The results obtained were essentially the same as Thornton's (17).

Tests on Urinary Output of Ascorbic Acid

Estimations of vitamin C in the urine of several residents were carried out for the purpose of correlating the output of vitamin C with the dietary intake. This was done in the latter part of January, 1940, and again in the latter part of September, 1940. During the summer the subjects were not all in continuous residence at Athabasca Hall.

The amount of ascorbic acid excreted was determined on one day and again on the next day after the administration of a 200 mg. test dose of pure ascorbic acid. The tests were carried out on 24 hr. specimens, collected in brown bottles, and preserved with a mixture of 5 ml. of 20% metaphosphoric acid and 15 ml. of concentrated hydrochloric acid. The titrations were done on the day of the final collection for the 24 hr. period.

The method used for the estimation of vitamin C in urine was a modification of that of Abbasy, Harris, *et al.* (1). The dye solution was a 1 : 10 dilution of that used for the plant titrations; 1 ml. = approximately 0.020 mg. of vitamin C. It was restandardized after dilution. This dilution of the dye is stable for not more than two days. It was run in from a 10 ml. burette into 5-ml. urine samples (diluted with 10 ml. of hydrochloric-metaphosphoric acid mixture) until a definite pink colour persisted for 10 sec.

An average percentage recovery of 96.5 of added ascorbic acid was obtained by this method. If, instead, the urine was run into a known quantity of dye, inconsistent results and low percentage recoveries were obtained. This error was due to the presence of other reducing substances in the urine, which have a greater opportunity to react with the dye.

Results

For 12 months the diet of residents of Athabasca Hall was investigated. The bar graph (Fig. 1) shows clearly the variation per month in intake, and the effect that removal of citrus fruits (grapefruit and oranges) from the diet would have.

For the months from November to May, inclusive, the average daily intake was found to be 41 mg. From June to October, inclusive, it was 82 mg.

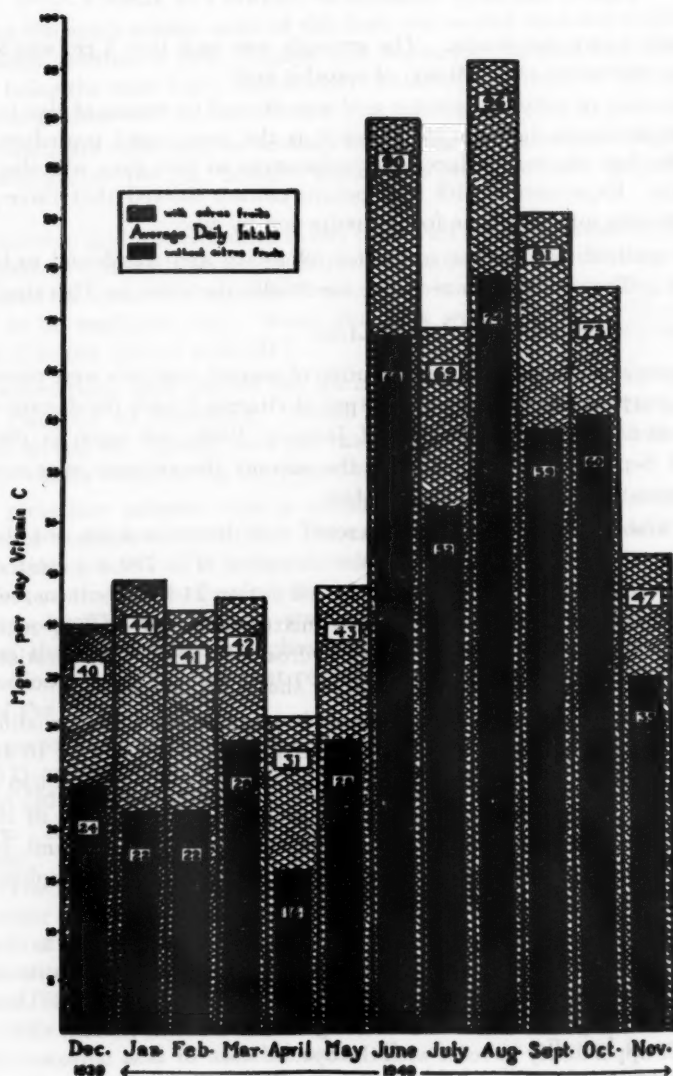


FIG. 1. Average daily intake of vitamin C, Athabasca Hall dietary.

The intake of vitamin C in June is high, because of the abundant supply of fresh strawberries. The value for July is 21 mg. less, but is still high because of the fresh tomatoes and other fresh vegetables then coming into use. The highest intake is in August, owing to the increased vitamin C content of potatoes, cabbage, cauliflower and tomatoes, the vitamin C content of which is then about at its peak. The intake in September and October drops slightly,

and November shows a definite decline, owing mainly to loss of ascorbic acid in vegetables on storing and the omission of fresh and canned tomatoes during the week of the test. In April the lowest values for potatoes and oranges were recorded, and no tomatoes were eaten during the week, all of which accounts partly for the daily intake being the least in April.

Urinalysis Results

The results obtained by different workers on the output of vitamin C as related to dietary intake and saturation of the tissues are many and varied (15). Abbasy *et al.* (1) state that an excretion of 10 to 15 mg. vitamin C in 24 hr. indicates a borderline intake, while Van Eekelen *et al.* (18) state that 40 mg. output per day indicates a liberal intake and saturation of the tissues. Johnson and Zilva (9) found that the excretion of vitamin C in the winter is almost nil, never greater than 10 to 15 mg. a day; but it rose after the summer.

In January the average amount excreted was 17 mg. a day (Table I). In Table II, although the average is 14.3 mg. per day, only one output falls below 10 mg. and four of the seven exceed 15 mg. In Table III, however, the average amount excreted by students tested in March was only 7.4 mg. This

TABLE I
URINARY OUTPUT OF VITAMIN C BY ATHABASCA HALL RESIDENTS

| Subject | Vitamin C excreted, mg./24 hr. | | |
|--------------------------------|--------------------------------|------------------------------|--------------------|
| | Before test dose | After test dose | Per cent excreted* |
| <i>January 20 - 21, 1940</i> | | | |
| E.O.L. | 20.9 | 15.6 | 0.0 |
| L.T. | 17.8 | 17.6 | 0.0 |
| L.B.P. | 15.1 | 21.0 | 3.0 |
| E.H.B. | 16.3 | 24.6 | 2.1 |
| J.H.W. | 17.1 | (after 400 mg. dose) 17.3 | 0.1 |
| W.W.P. | 14.8 | 18.6 | 1.9 |
| Average | 17.0 | 19.1 | 1.05 |
| <i>September 27 - 28, 1940</i> | | | |
| E.O.L. | 23.2 | 65.9 | 21.4 |
| L.T. | 54.8 | 195.1 | 70.2 |
| L.B.P. | 27.4 | 23.3 | 0.0 |
| E.H.B. | 42.6 | 117.8 | 37.6 |
| J.H.W. | 43.7 | 86.4 | 21.4 |
| W.W.P. | 23.7 | 37.3 | 6.8 |
| Average | 35.9 | 87.6 | 25.9 |

* The percentage excreted is calculated as follows:

$$\frac{\text{Test dose output} - \text{normal output}}{\text{Test dose (200 mg.)}} \times 100 = \% \text{ excreted.}$$

TABLE II
URINARY OUTPUT OF VITAMIN C BY MALE SUBJECTS TESTED ONLY IN JANUARY
January 23 - 24, 1940

| Subject | Vitamin C excreted in mg./24 hr. | | |
|---------|----------------------------------|-----------------|-------------------|
| | Before test dose | After test dose | Per cent excreted |
| J.L. | 12.0 | 66.5 | 27.3 |
| A.C.G. | 18.4 | 40.6 | 11.1 |
| H. | 7.9 | 16.6 | 4.4 |
| F.D. | 18.4 | 19.6 | 0.6 |
| A.E.R. | 15.1 | 16.2 | 0.6 |
| F.W. | 11.1 | 11.4 | 0.2 |
| A.C.W. | 16.9 | 13.4 | 0.0 |
| Average | 14.3 | 26.3 | 6.0 |

TABLE III
URINARY OUTPUT OF VITAMIN C IN MG./24 HR.

| March 14, 1940 | | December 5, 1940 |
|------------------------------|--|--------------------------------|
| Normal output level, Group I | Output after 200 mg. test dose, Group II | Normal output level, Group III |
| 2.6 | 2.4 | 8.7 |
| 3.3 | 3.7 | 12.5 |
| 3.4 | 4.3 | 15.0 |
| 3.9 | 4.6 | 15.2 |
| 4.3 | 5.0 | 15.4* |
| 5.1 | 6.6 | 15.5 |
| 5.3 | 6.8 | 16.8 |
| 5.4* | 7.1 | 16.9 |
| 5.4 | 7.1 | 17.0 |
| 5.4 | 7.7 | 17.1 |
| 5.4 | 8.2 | 17.3 |
| 5.9 | 8.9* | 17.4 |
| 6.2 | 10.2* | 18.0 |
| 6.4* | 10.3 | 18.3 |
| 6.4 | 14.2* | 18.7 |
| 6.8 | 14.7 | 19.1 |
| 7.0 | 16.3 | 19.6 |
| 8.4* | 36.0 | 19.6 |
| 8.5 | 46.6 | 19.8 |
| 8.7* | 70.8 | 20.1 |
| 8.7 | 73.7 | 20.2 |
| 9.0 | 86.0 | 20.8 |
| 9.0 | 93.8 | 21.7 |
| 12.2 | | 23.6 |
| 12.3 | | 24.8 |
| 12.6 | | 27.0* |
| 24.6 | | 27.5 |
| | | 29.1 |
| Average 7.4 mg./day | 23.7 mg./day | 19.1 mg./day |

* Residents of Athabasca Hall.

drop in average output from January to March may be accounted for in part by individual variation, but would more likely be due to decreased intake (Fig. 1) and gradual depletion of the body stores.

Even after a 200 mg. test dose, Group II showed an average output of only 23.7 mg. per day, that of 73.9% of the subjects being below this average figure.

The state of saturation of the tissues is indicated more clearly by the output after a test dose. Baumann (2) estimated that 60 to 80% of the test dose will be excreted in 24 hr. by a healthy person whose tissues are saturated. In January (Tables I and II) these figures are not nearly approximated. September however presents a better picture, with the average output before the test dose doubled, that after the test dose four times greater, and the average percentage of vitamin C excreted many times increased. Even so, only L.T. and E.H.B. come within range of percentage output estimated by Baumann, taking into consideration that Baumann estimates the percentage on total output figures, not on the difference between the output level before and after the test dose.

In December (Table III) the average amount-excreted by Group III is 19.1 mg.—three times the output in March. This is indicative of increased body stores, as are the higher outputs obtained in September. As can be seen from the tables, the total and percentage output vary greatly with the different individuals. The 200 mg. ingested by L.B.P. (Table I) was, then, either absorbed and taken up by the tissues or was destroyed in the gastro-intestinal tract. Blood analyses would indicate which of these processes actually occurred. Similar examples can be found in Table II. It seems evident that different individuals have different saturation capacities, and that an estimation of the normal output cannot always be a true indication of the saturation of the tissues. Determination of the output after a test dose is a better means of determining saturation. However, a single estimation of urinary vitamin C is valuable in distinguishing extreme deficiency. It is also useful in a survey of adequacy in a large group of persons.

Discussion

From the tables presented it can be seen that the tissues of persons subsisting on a diet that supplies an average daily intake of 41 mg. of vitamin C per day are not nearly saturated, according to the data obtained in determining output after a test dose. As this intake is increased to an 82 mg. average, the amount excreted also increases in simple relation, but only two persons out of six showed saturation. If tissue saturation is the true criterion of optimum vitamin C utilization, then it seems that even the well supervised, large-scale cooking methods studied here do not supply an adequate amount of vitamin C. Also, if tissue saturation measured by a test dose of 200 mg. is the criterion, the daily requirement must be very high.

Acknowledgments

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THE REACTION OF HYDROGEN ATOMS WITH ISOBUTANE¹

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Abstract

The reaction of hydrogen atoms with isobutane has been investigated by the Wood-Bonhoeffer discharge tube method, over a temperature range 30° to 250° C. An activation energy of 10.5 ± 1.5 kcal. was obtained for the reaction.

The nature of the products at a given temperature was found to depend upon the concentration of hydrogen atoms present. With low atom concentrations (5 to 9%) methane was essentially the only product at temperatures below 170° C. At 250° C., ethane was formed to the extent of approximately one-half the amount of methane. With higher atom concentrations (14 to 24%) ethane was formed in appreciable quantities at 140° to 170° C., and exceeded the methane content at 250° C. Small amounts of propane were formed at the higher temperatures.

The results at low temperatures appear to be satisfactorily explained by assuming a primary dehydrogenation reaction:



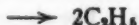
followed by a series of "atomic cracking" reactions. To account for the behaviour at higher temperatures, additional secondary reactions, involving decomposition of radicals and their reaction with molecular hydrogen, are assumed.

Introduction

Reactions between hydrogen atoms and the lower normal paraffin hydrocarbons have been studied extensively. It is assumed generally that the primary step is abstraction of a hydrogen atom from the hydrocarbon molecule, followed by a series of "atomic cracking" reactions. Thus, the reactions postulated for normal butane (12) are:



followed at low temperatures by:



At higher temperatures, additional secondary reactions are assumed.

No investigation of the reaction between hydrogen atoms and isobutane has been reported previously. A study of this reaction was of interest, not only to obtain additional information about the elementary reactions of the hydrocarbons in the presence of hydrogen atoms, but also to enable comparison of the behaviour of a branched chain molecule with that of the straight chain hydrocarbons previously investigated.

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Experimental

The reaction was studied by the Wood-Bonhoeffer method, in an apparatus similar essentially to that described previously by Steacie (11).

Commercial hydrogen was purified by passage over platinized asbestos at 500° C., through a drying tube and a liquid-air cooled trap to remove water and finally through a trap containing silica gel cooled in liquid air to remove traces of methane found to be present. This dry hydrogen was used in several experiments. In others, the purified gas was moistened by passage over water in a trap at room temperature. The hydrogen was admitted to the reaction vessel through a calibrated flowmeter, the pressure at the inlet of the flowmeter being maintained at atmospheric by a mercury blow-off valve.

Isobutane was obtained from the Ohio Chemical and Manufacturing Company. It was specified to be 99% pure, with *n*-butane the only impurity. It was used after a single low-temperature fractionation. The isobutane flow rate was regulated by adjusting the pressure on the supply side of a capillary flowmeter.

Hydrogen atoms were formed in a high voltage discharge tube, consisting of a Pyrex tube, 2.5 cm. in diameter, to which were sealed two side tubes each containing an aluminium electrode. Connection to the electrodes was made with heavy platinum wires which passed out of the electrode chambers through capillary tubes and DeKhotinsky seals. The discharge was operated with 2500 volts across the tube and a 5000 ohm resistance. The operating current was kept at 200 milliamperes by a rheostat in the primary circuit of the transformer.

The reaction chamber was a Pyrex tube 7 cm. in diameter, with a volume of 895 ml. It was situated close to the discharge to minimize hydrogen atom recombination prior to reaction. The chamber was surrounded by an electric furnace, the temperature of which was manually controlled to within 2° C. The isobutane inlet tube and a thermocouple well were sealed into the reaction vessel from below.

The wall of the reaction chamber was poisoned with phosphoric acid to enable a suitable concentration of hydrogen atoms to be maintained with a stream of dry hydrogen. When moist hydrogen was used, the additional poisoning action gave an atom concentration two to three times that secured with dry hydrogen.

The products of reaction, together with unchanged isobutane and hydrogen, were drawn from the reaction vessel by a high-speed diffusion pump backed by an oil pump. The reaction time was varied between 0.40 and 0.91 sec. A liquid-air cooled trap between the reaction vessel and the diffusion pump served to remove unchanged isobutane, higher hydrocarbons if present, and the major portion of any propane, ethane, or ethylene. The remainder of the gas stream passed through the diffusion pump and through a liquid-air cooled trap containing silica gel to remove methane.

After each experiment, which lasted 2–2.5 hours, the reaction products were removed to a gas holder and analysed on a low temperature distillation unit of the Podbielniak type. The hydrogen–methane fraction was analysed by combustion. In addition to the distillation, the content of unsaturates in some samples was determined by absorption in a bromine–potassium-bromide solution.

The hydrogen atom concentration in the reaction vessel was measured at each working temperature with a Wrede diffusion gauge. The pressure differential set up by atom recombination in the capillary of this instrument was determined with a Pirani gauge. The values obtained for the hydrogen atom concentration would be higher than those existing during an experiment when the concentration of atoms is reduced by reaction. Correction was made for a pressure differential in the gauge, arising from thermal effects, by making measurements at each temperature without the discharge tube in operation.

Results

The experimental conditions employed and the analytical data obtained are given in Table I.

The number of collisions per second of an isobutane molecule with hydrogen atoms was calculated from the expression (7, p. 46):

$$Z_{C_4H_{10} \cdot H} = 2\sqrt{2\pi} \left(\frac{d_H + d_{C_4H_{10}}}{2} \right)^2 \left(\frac{M_H + M_{C_4H_{10}}}{M_H \cdot M_{C_4H_{10}}} \cdot RT \right)^{1/2} \cdot N_H,$$

where d_H and $d_{C_4H_{10}}$ are the molecular diameters,

M_H and $M_{C_4H_{10}}$ are the molecular weights,

N_H is the number of hydrogen atoms per ml.,

and R and T are the gas constant and the absolute temperature respectively. The value of d_H was taken as 2.14×10^{-8} cm. (1) and that of $d_{C_4H_{10}}$ as 4.66×10^{-8} cm. (18).

The activation energies were calculated from the relation

$$\text{Collision yield} = A \cdot e^{-E/RT},$$

assuming a value of 0.1 for the steric factor, A . This steric factor, while possibly too large (6, 8), was taken to facilitate comparison between the results of this investigation and others of a similar type, where the value 0.1 has been used.

The data necessary for the calculation of the activation energies and the values obtained are given in Table II.

Discussion

Comparison of the collision yields for isobutane with those for normal butane (12) shows that the hydrogen atom reaction with isobutane is of the order 10 times slower than that with normal butane (Table II). In fact, the rate of the isobutane reaction is approximately the same as that of propane (13). Apparently, the branched chain of isobutane offsets any tendency

TABLE I
EXPERIMENTAL CONDITIONS AND PRODUCTS FORMED IN THE REACTION OF ISOBUTANE WITH HYDROGEN ATOMS

| Run No. | Temp., °C. | Press., mm. | Atom conc., % | Condition of hydrogen | Flow, moles/sec. $\times 10^4$ | | Products, mole % | | | | Butane reacted, % |
|---------|------------|-------------|---------------|-----------------------|--------------------------------|--------------------------------|------------------|-------------------------------|-------------------------------|--------------------------------|-------------------|
| | | | | | H ₂ | C ₄ H ₁₀ | CH ₄ | C ₂ H ₆ | C ₃ H ₈ | C ₄ H ₁₀ | |
| 1 | 32 | 0.36 | 9.1 | Dry | 1.54 | 0.245 | 11.9 | — | — | 88.1 | 3.4 |
| 2 | 31 | 0.36 | 9.1 | Dry | 1.54 | 0.250 | 11.7 | — | — | 88.3 | 3.2 |
| 3 | 32 | 0.36 | 9.1 | Dry | 1.54 | 0.246 | 12.7 | — | — | 87.3 | 3.5 |
| 4 | 32 | 0.33 | 24.2 | Moist | 1.82 | 0.434 | 7.1 | Trace | Trace | 92.9 | 1.9 |
| 5 | 33 | 0.33 | 24.2 | Moist | 1.82 | 0.450 | 7.2 | Trace | Trace | 92.8 | 1.9 |
| 6 | 101 | 0.36 | 8.2 | Dry | 1.54 | 0.239 | 12.0 | — | — | 88.0 | 3.3 |
| 7 | 101 | 0.36 | 8.2 | Dry | 1.54 | 0.247 | 11.0 | — | — | 89.0 | 3.0 |
| 8 | 100 | 0.36 | 8.2 | Dry | 1.54 | 0.245 | 13.9 | — | — | 86.1 | 3.9 |
| 9 | 101 | 0.36 | 8.2 | Dry | 1.54 | 0.245 | 14.0 | — | — | 86.0 | 3.9 |
| 10 | 101 | 0.36 | 8.2 | Dry | 1.54 | 0.239 | 13.7 | — | — | 86.3 | 3.8 |
| 11 | 141 | 0.32 | 17.3 | Moist | 1.82 | 0.445 | 6.2 | 0.7 | Trace | 93.1 | 2.0 |
| 12 | 140 | 0.32 | 17.3 | Moist | 1.82 | 0.440 | 5.3 | 0.6 | Trace | 94.1 | 2.0 |
| 13 | 171 | 0.36 | 7.1 | Dry | 1.54 | 0.251 | 13.7 | Trace | Trace | 86.3 | 3.8 |
| 14 | 171 | 0.36 | 7.1 | Dry | 1.54 | 0.245 | 13.5 | Trace | Trace | 86.5 | 3.8 |
| 15 | 172 | 0.36 | 7.1 | Dry | 1.54 | 0.245 | 12.9 | Trace | Trace | 87.1 | 3.6 |
| 16 | 171 | 0.36 | 7.1 | Dry | 1.54 | 0.249 | 13.4 | Trace | Trace | 86.6 | 3.7 |
| 17 | 170 | 0.32 | 7.1 | Dry | 1.82 | 0.220 | 4.8 | Trace | Trace | 95.2 | 1.6 |
| 18 | 170 | 0.32 | 16.0 | Moist | 1.82 | 0.218 | 5.2 | 3.6 | 1.1 | 90.1 | 4.2 |
| 19 | 250 | 0.33 | 5.6 | Dry | 1.82 | 0.225 | 7.4 | 3.7 | — | 88.9 | 4.0 |
| 20 | 250 | 0.34 | 13.9 | Moist | 1.82 | 0.408 | 6.5 | 9.0 | 1.8 | 82.7 | 8.5 |
| 21 | 250 | 0.35 | 13.9 | Moist | 1.82 | 0.417 | 6.4 | 8.0 | 1.8 | 83.8 | 7.6 |
| 22 | 250 | 0.32 | 13.9 | Moist | 1.82 | 0.242 | 12.4 | 14.9 | Trace | 72.7 | 12.6 |

TABLE II
DATA FOR COLLISION YIELDS AND ACTIVATION ENERGIES IN THE REACTION OF ISOBUTANE WITH HYDROGEN ATOMS

| Run No. | Temp., °C. | Total flow corrected for hydrogen atoms, moles sec. $\times 10^3$ | Reaction time, sec. | Partial press. of hydrogen atoms, mm. | $Z_{\text{C}_4\text{H}_{10}\cdot\text{H}}$ per sec. $\times 10^{-4}$ | $Z_{\text{C}_4\text{H}_{10}\cdot\text{H}}$ in reaction time $\times 10^{-4}$ | Butane reacted, % | Collision yield $\times 10^4$ | E, kcal, assuming $A = 0.1$ |
|---------|------------|---|------------------------|--|--|---|----------------------|----------------------------------|-----------------------------------|
| 1 | 32 | 1.86 | 0.91 | 0.033 | 9.73 | 8.84 | 3.4 | 3.85 | 9.0 |
| 2 | 31 | 1.86 | 0.91 | 0.033 | 9.73 | 8.84 | 3.2 | 3.62 | 9.0 |
| 3 | 32 | 1.86 | 0.91 | 0.033 | 9.73 | 8.84 | 3.5 | 3.96 | 8.9 |
| 4 | 32 | 2.47 | 0.63 | 0.080 | 23.6 | 14.8 | 1.9 | 1.28 | 9.6 |
| 5 | 33 | 2.49 | 0.62 | 0.080 | 23.5 | 14.6 | 1.9 | 1.30 | 9.6 |
| 6 | 101 | 1.84 | 0.75 | 0.029 | 7.47 | 5.62 | 3.3 | 5.88 | 10.7 |
| 7 | 101 | 1.85 | 0.75 | 0.029 | 7.47 | 5.62 | 3.0 | 5.34 | 10.7 |
| 8 | 100 | 1.85 | 0.75 | 0.029 | 7.47 | 5.62 | 3.9 | 6.94 | 10.6 |
| 9 | 101 | 1.85 | 0.75 | 0.029 | 7.47 | 5.62 | 3.9 | 6.94 | 10.6 |
| 10 | 101 | 1.84 | 0.75 | 0.029 | 7.47 | 5.62 | 3.8 | 6.76 | 10.6 |
| 11 | 141 | 2.42 | 0.46 | 0.055 | 14.0 | 6.44 | 2.0 | 3.10 | 12.3 |
| 12 | 140 | 2.42 | 0.47 | 0.057 | 14.5 | 6.86 | 2.0 | 2.92 | 12.3 |
| 13 | 171 | 1.85 | 0.63 | 0.025 | 5.52 | 3.50 | 3.8 | 10.8 | 12.1 |
| 14 | 171 | 1.84 | 0.63 | 0.025 | 5.52 | 3.50 | 3.8 | 10.8 | 12.1 |
| 15 | 172 | 1.84 | 0.63 | 0.025 | 5.52 | 3.50 | 3.6 | 10.3 | 12.2 |
| 16 | 171 | 1.84 | 0.63 | 0.025 | 5.52 | 3.50 | 3.7 | 10.6 | 12.2 |
| 17 | 170 | 2.10 | 0.49 | 0.023 | 5.56 | 2.74 | 1.6 | 5.84 | 12.7 |
| 18 | 170 | 2.18 | 0.48 | 0.051 | 12.5 | 5.95 | 4.2 | 7.06 | 12.5 |
| 19 | 250 | 2.10 | 0.43 | 0.018 | 4.17 | 1.81 | 4.0 | 22.1 | 13.5 |
| 20 | 250 | 2.35 | 0.40 | 0.048 | 10.7 | 4.26 | 8.5 | 20.0 | 13.7 |
| 21 | 250 | 2.36 | 0.41 | 0.049 | 11.0 | 4.47 | 7.6 | 17.0 | 13.8 |
| 22 | 250 | 2.19 | 0.40 | 0.044 | 10.0 | 4.03 | 12.6 | 31.3 | 13.2 |

towards increased reactivity with increasing molecular weight (4, 19), such as is observed between propane and normal butane.

The values of the activation energy of the isobutane reaction are higher than those found for normal butane at corresponding temperatures (Table II). It may be assumed that at least part of the observed increase of activation energy with increased temperature is only apparent, and is the result of error in the assumed atom concentration at higher temperatures where the increased amount of reaction might be expected to cause a relatively greater lowering of the stationary hydrogen atom concentration. Part of the increase in E might, however, be the result of a decreased steric factor brought about, for example, by increased rotation of the molecule, or increased oscillation of alkyl groups at the higher temperatures. Giving somewhat greater weight to the lower temperature values, the activation energy for the reaction of hydrogen atoms with isobutane may be taken as 10.5 ± 1.5 kcal.

The relative amounts of ethane and methane at a given temperature, at the higher temperatures, were dependent upon whether dry or moist hydrogen was used (Table I). Using dry hydrogen, only traces of ethane were found at temperatures up to 170°C ., and the methane content exceeded the ethane at 250°C . Using moist hydrogen, the amount of ethane became appreciable between 140° to 170°C ., and surpassed the methane content at 250°C . If, as seems highly probable (3, p. 153, 11), the only significant effect of using moist hydrogen is to increase the hydrogen atom concentration, the results indicate clearly that the nature of the products at a given temperature in discharge tube studies may depend largely upon the hydrogen atom concentration.

These data may be compared with the results reported for the same reaction with normal butane (12). At 35°C ., normal butane yielded methane exclusively, with appreciable quantities of ethane appearing when the temperature was raised to 100°C . The ratio of ethane to methane increased rapidly with increasing temperature until at 250°C . there was approximately twice as much ethane as methane in the products. Analysis showed that propane was not produced at any temperature.

Thus the behaviour of isobutane using moist hydrogen, i.e., at the higher atom concentrations, is analogous to that reported for normal butane using dry hydrogen and with atom concentrations considerably smaller than those obtained in the present study under similar conditions. This fact was thought at first to indicate a marked difference between the two reactions. An experiment was therefore made with normal butane, at 32°C . using dry hydrogen, corresponding to 9.1% of hydrogen atoms, and with flow rates similar to those used previously with normal butane (12). The sole product was found to be methane, in agreement with the earlier study, but the amount of reaction was approximately one-half that reported previously. On the other hand, a single experiment with propane, also using dry hydrogen at 35°C ., and with flow rates comparable to those used by Steacie and Parlee (13) gave results which agreed with their data with respect to the products

formed and to the hydrogen atom concentrations used, as estimated from the relative amounts of reaction. It seems possible, therefore, that the hydrogen atom concentrations actually present during the normal butane study were considerably higher than reported. While an error in the atom concentration, even several-fold, would not materially affect the conclusions drawn, it would mean that the data for normal butane should be compared with those for isobutane at the higher atom concentrations. The only difference in the general behaviour of the two compounds, apart from reactivity, apparently then would be the presence, particularly at higher temperatures, of small amounts of propane in the products from isobutane.

Any attempt to formulate a mechanism for the reaction of isobutane with hydrogen atoms must take into account the presence of methane alone in the products at low temperatures, the presence of ethane and small amounts of propane at higher temperatures, and the dependence of the relative amounts of the major products on hydrogen atom concentration.

The Primary Reaction

The possible primary steps are:

(a) *Hydrogen abstraction:*



This type of reaction has been postulated for hydrogen atom reactions with other hydrocarbons (12, 13, 14). It does not seem possible, on the basis of available information, and in view of the uncertainty in assigning a steric factor, to establish whether this reaction should correspond to removal of a primary, or the tertiary, hydrogen atom of the molecule.

(b) *Chain breaking:*

The chain breaking reactions which may be postulated for the primary step are:



If the first of these occurred, considerable propane should have been present in the products at low temperatures. Since propane was not found in measurable quantities except at 250° C., this reaction may be ruled out as the primary step. By analogy, the second reaction may also be ruled out. Moreover, such reactions are analogous to:



for which the activation energy has been estimated as approximately 30 kcal. The fact that the chain breaking would occur at a tertiary carbon atom in isobutane probably would not decrease the activation energy appreciably, and any reaction of this type can probably be excluded as the primary step. The abstraction of a hydrogen atom would thus appear to be the primary reaction.

Secondary Reactions

At temperatures between 30° and 140° C. the only product found in appreciable amount was methane. This behaviour is explained most readily

by assuming a series of "atomic cracking" reactions subsequent to the primary step, as first suggested by Rice and Teller (10) and elaborated subsequently by Taylor (16). Regardless of whether a primary, or the tertiary, hydrogen atom is abstracted in the primary step, the first of these reactions presumably forms the isopropyl radical:



which may be followed by:

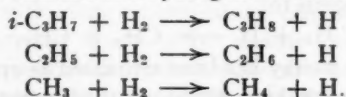


This last reaction was originally suggested to account for the formation of methane in the reaction of hydrogen atoms with ethane (10). The activation energy has been estimated to be about 5 kcal. A similar value is probable for the reaction of the isopropyl radical with hydrogen atoms. The occurrence of such reactions has received considerable experimental (12, 13) and theoretical (6, 10) support.

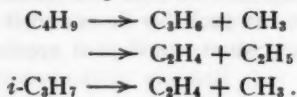
Reactions of radicals with hydrogen molecules apparently do not occur at the lower temperatures since, with the exception of methyl radicals, the products should be ethane, propane, etc., which were not found in significant amounts below the temperature range 140° to 170° C. This is in agreement with recent investigations which indicate that the reaction of methyl radicals with molecular hydrogen does not have a measurable rate below about 160° C. (9, 17). Radical recombination reactions also appear to play virtually no part in the over-all changes, since these too should give rise to products other than methane at low temperatures. Presumably the concentration of hydrogen atoms was so much greater than that of radicals that the "atomic cracking" reactions occurred almost exclusively. The traces of ethane and propane found at the lower temperatures probably represent the maximum extent to which recombination of radicals occurred.

Above 140° C., or 170° C., depending upon the hydrogen atom concentration, appreciable quantities of ethane appeared in the products. In the higher temperature range reactions of radicals with molecular hydrogen and radical decomposition reactions might be expected to become increasingly prominent.

Reactions between radicals and hydrogen molecules might occur as follows:



The probable radical decomposition reactions would seem to be:



Any unsaturate formed must have been hydrogenated rapidly, since none was detected in the analyses of the products.

The increase in the ethane : methane ratio observed with increased hydrogen atom concentration at the higher temperatures apparently cannot be explained on the basis of a reaction between hydrogen atoms and propylene. This reaction has been studied by the discharge tube method (2), and found to yield methane, ethane, and propane. Preliminary work indicates, however, that as the hydrogen atom concentration is increased relative to that of propylene the proportion of methane to ethane increases; this is the reverse of the behaviour observed in the isobutane reaction. Similarly, it seems likely that an increased methane : ethane ratio would accompany an increase in the relative hydrogen atom concentration in the corresponding reaction with ethylene. This point is being investigated at the present time.

The increase in the proportion of ethane in the products, with increase in the hydrogen atom concentration at the higher temperatures probably results from an increased production of ethyl radicals, which undergo reaction with hydrogen molecules at these temperatures to form ethane according to (cf. (13)):



or possibly by a ternary collision, as suggested (15) for the corresponding reaction of methyl radical:



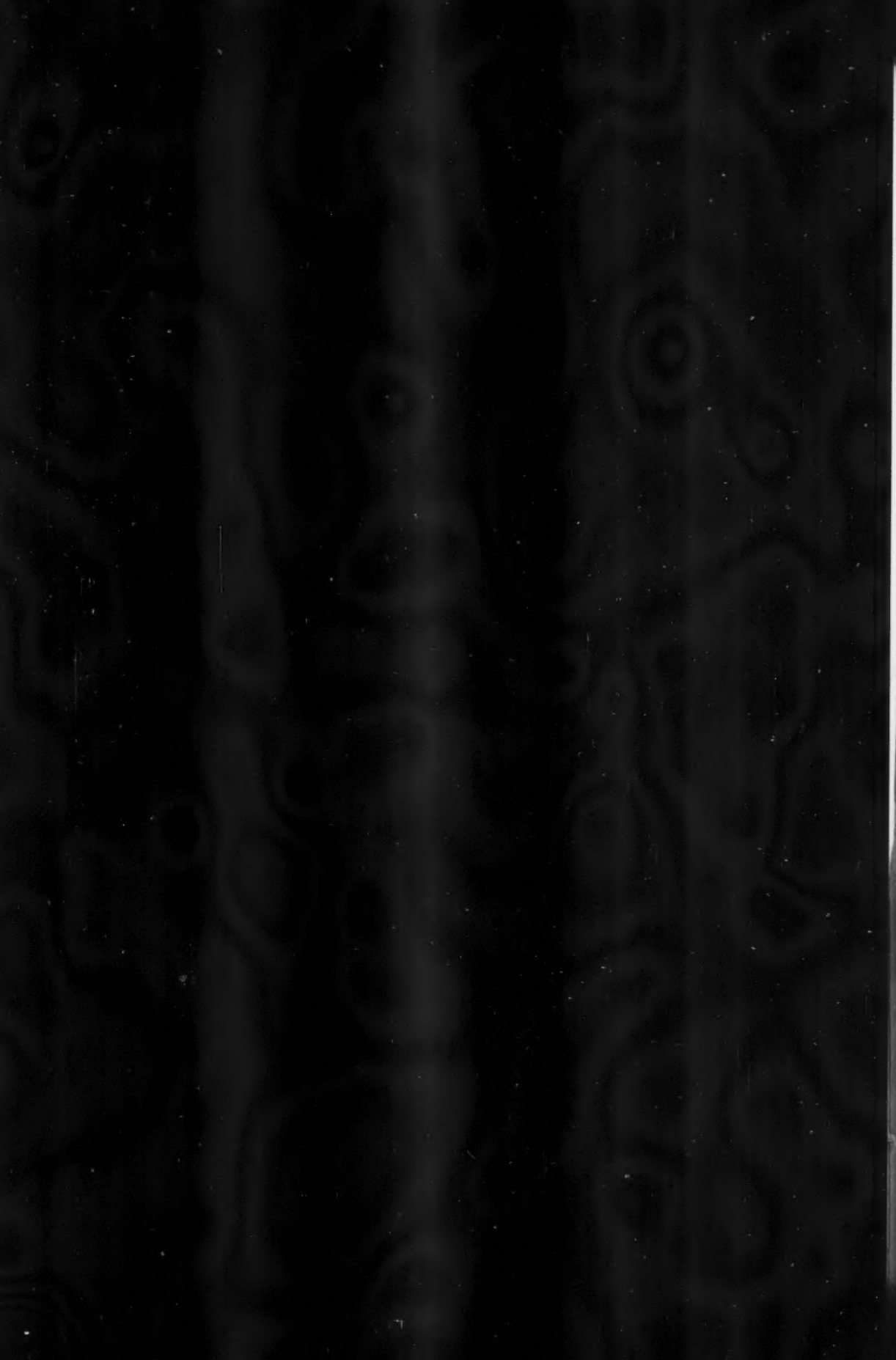
While the reaction of methyl radicals with hydrogen molecules should also gain in prominence at the higher temperatures, the relative extent to which methyl radicals are produced from ethyl radicals by the action of hydrogen atoms might be expected to be diminished as a result of ethane formation.

The presence of some propane in the reaction of isobutane with hydrogen atoms, in contrast with its absence in the normal butane reaction, is explicable if it is accepted that normal butane produces normal propyl, and isobutane produces isopropyl radicals. The absence of propane in the reaction products with normal butane has been explained by assuming that the reaction of propyl radicals with hydrogen molecules occurs at an appreciable rate only at a temperature higher than that at which the radicals are destroyed before they can react (12). The isopropyl radical appears to be slightly more stable than the normal propyl radical (5). Some propane might be produced, therefore, by the reaction of isopropyl radicals with molecular hydrogen at higher temperatures.

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